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MN Pollution Control Agency  
Duluth, MN

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August 25, 2015

Mr. John Thomas  
Pollution Control Specialist Senior  
Compliance and Enforcement Section, Industrial Division  
Minnesota Pollution Control Agency (MPCA)  
525 Lake Avenue South, Suite 400  
Duluth, MN 55802

**RE: Minntac Tailings Basin Groundwater Sulfate Reduction Plan  
Pilot Study Design for Selected Alternatives**

Dear Mr. Thomas:

Pursuant to the January 2014 revision of the Minntac Tailings Basin Groundwater Sulfate Reduction Plan (GWSRP), U. S. Steel is submitting this letter to inform MPCA of the status of the pilot study design for the selected alternatives. As indicated in an April 25, 2014 letter to you regarding Selection of Alternatives for Further Investigation related to the GWSRP, U. S. Steel has chosen to evaluate implementation of in-situ bio-chemical sulfate reduction that utilizes zero valent iron (ZVI) or addition of organic substrates, in combination with the existing seep collection and return system, as a means to achieve compliance with the groundwater sulfate standard at its property boundary near MW12 (focus area).

#### **Background**

Biochemical reduction of sulfate is a common method for reducing sulfate in groundwater. Commonly, organic substrates are used to stimulate sulfate reduction. The use of ZVI has been demonstrated to enhance sulfate reduction. The benefits of using ZVI as the predominant amendment, or possibly even the sole amendment, are that ZVI has much greater longevity and is easier to control during placement in the subsurface. Additionally, ZVI provides a continuing source of Fe<sup>2+</sup>, which sequesters free sulfide species that are generated during sulfate reduction thereby preventing their migration.

One approach to be evaluated in the proposed pilot-scale study is the decoupling of ZVI from an additional organic substrate—first, by monitoring and evaluating sulfate reduction using ZVI alone, and if necessary, adding an injectable carbon source downgradient of the installed ZVI. This conceptual approach is shown on Figure 1. This phased approach would allow for a very controlled shift in subsurface geochemistry in such a way as to target a very specific range of geochemical conditions. To accomplish this, ZVI would first be installed in the subsurface such that groundwater flow through the ZVI will create a downgradient reactive zone enriched with dissolved hydrogen. The dissolved hydrogen in this zone can be utilized by the native microbial community directly to reduce sulfate and it also provides the reducing conditions necessary for sulfate reducing bacteria (SRBs) to thrive. The downgradient reactive zone would then be monitored for generation of conditions conducive to efficient sulfate reduction. Geochemical modeling and prior experience indicate that the target conditions consist of a reduction potential (Eh) of between -100 and -200 millivolts (mV) and a pH between 8 and 9. In order to achieve the desired level of sulfate reduction (and concomitant cell growth), dissolved carbon will be added as necessary in the downgradient reactive zone independent of the ZVI installation.

The objectives for the proposed pilot-scale study are as follows:

- Develop design parameters for construction of a full-scale system using ZVI as the sole and/or primary electron donor for driving in-situ sulfate reduction.
- Evaluate the constructability of a subsurface ZVI system in the focus area and select a reasonable alignment and size of a full-scale system to meet required performance criteria.
- Develop an appropriate performance and maintenance monitoring program using design considerations and site characteristics.
- Evaluate potential impact of site-specific factors (including extreme temperature conditions) on treatment effectiveness.

#### **Conceptual Design of Pilot-scale System**

To meet the objectives listed above, the proposed approach for the pilot-scale study is to construct three test cells to evaluate differing methods for installation of ZVI in the subsurface. The proposed test cells would be separated by driven sheet piles and are described below. Figure 2 shows the layout of the pilot-scale test cells along with a proposed monitoring well network. Figure 3 shows the proposed pilot-scale test cells in plan and profile views with proposed dimensions. However, the final dimensions and layout of the pilot-scale test cells are subject to change during the engineering design and/or construction phases of this work.

1. **Shallow ZVI Wall** – The middle test cell would consist of a shallow excavated trench backfilled with 15-20% ZVI/sand mixture with a cap consisting of two feet of hydrated bentonite to create a permeable ZVI “wall”. Excavation and backfilling would be aided by installation of two temporary sheet piles driven at the upgradient and downgradient faces of the trench, which would be removed after emplacement of the ZVI/sand mixture and bentonite cap. The resulting permeable ZVI wall would include a minimum of three two-inch piezometers to allow monitoring of groundwater conditions (hydraulic and geochemical) within the wall itself.
2. **Deep ZVI Borings** – Next to the shallow ZVI wall would be a test cell consisting of a gallery of ten 8- to 12-inch diameter borings advanced down to bedrock using rotosonic drilling methods, which were used with success to reach bedrock during recent field investigation activities. The borings would be backfilled with 15-20% ZVI/sand mixture with a top seal consisting of a minimum of two feet of hydrated bentonite.
3. **Deep ZVI Injection** – On the other side of the shallow ZVI wall, opposite the deep ZVI borings would be a test cell consisting of a gallery of three 6-inch diameter borings advanced down to bedrock for the injection of a colloidal form of ZVI (e.g., EHC®) or other injectable amendment identified during the column study.

A monitoring well network would be installed to monitor the hydraulic and geochemical performance of the test cells as shown on Figure 2; however, the monitoring well network and monitoring plan will need to be finalized as part of the final engineering design. The majority of the monitoring wells for the system are anticipated to be shallow 1-inch or 2-inch diameter piezometers that could be installed either with auger-drilling methods or possibly via direct-push tooling. Deep monitoring wells, where specified, will be drilled using rotosonic drilling methods. It is envisioned that dissolved oxygen, reduction potential, pH, and temperature, in addition to head pressure, will be measured in the monitoring wells on a routine, likely weekly, basis. Bio-Trap® samplers (Microbial Insights or equivalent) would also likely be deployed for quantifying SRBs and tracking microbial community structure over time in key wells. Sampling for sulfate and certain geochemical parameters would also be conducted routinely, the frequency of which would be guided by the data collection described above.

To more fully develop the information needed to complete a viable pilot-scale design, a second microcosm study has been undertaken, as well as a demonstration-scale column study. The next phase of the project includes evaluation of data from the Phase 2 microcosm and column studies, which will be used to finalize the proposed pilot-scale study plan. These efforts are already underway along with the preparation of the detailed engineering design of the pilot-scale system.

Based on the proposed location of the pilot testing, it appears that permits will be required for temporary and permanent impacts to wetlands in the vicinity. U. S. Steel is in the process of finalizing application materials to submit to the U. S. Army Corps of Engineers in order to initiate permitting activities.

If you have any questions or concerns regarding this matter, please contact me.

Sincerely,

A handwritten signature in black ink, appearing to read "Thomas A. Moe". The signature is fluid and cursive, with a long horizontal stroke extending to the left.

Thomas A. Moe  
Environmental Control Engineer  
Minnesota Ore Operations – Minntac  
United States Steel Corporation  
218-749-7485 – office

Enclosures

## Figures

## Install Zero Valent Iron in Subsurface



## Create Downgradient Reactive Zone

Eh +400 mV  
pH 6-7

6-8 Hg  
00 mV

## Optional Downgradient Carbon Addition



**Figure**



## Conceptual Approach for In-Situ Sulfate Reduction Using ZVI

## Minntac Tailings Basin

United States Steel Corporation

**Drafter: RS**

Date: 8/19/15

Contract Number: 03-33435B

Approved:

Revised: \_\_\_\_\_

**RAMBOLL** ENVIRON